Claims

- 1. An oxidizing system comprising the three components
- 5 a macrocyclic metal complex of the general formula (I)

$$\begin{array}{c|c}
 & Y_2 \\
 & O \\
 & N \\
 & N \\
 & N \\
 & R \\
 & O \\
 & O
\end{array}$$

$$\begin{array}{c}
 & Q \\
 &$$

10 where

- Y₁, Y₃ and Y₄ are each independently a single bond or a bridge member which contains 1, 2 or 3 carbon atoms in the bridge,
- 15 Y_2 is a bridge member having at least 1 carbon atom in the bridge,
 - R is independently in each occurrence hydrogen, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, phenoxy, CH₂CF₃ or CF₃ or two R radicals which are bound to the same carbon atom combine to form a substituted or unsubstituted benzene, cycloalkyl or cycloalkenyl ring, the carbon atom to which the two R radicals are bound being part of the benzene, cycloalkyl or cycloalkenyl ring,

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- M is a transition metal in the oxidation states I, II, III, IV, V or VI or is selected from groups 6, 7, 8, 9, 10 and 11 of the periodic table,
- 5 Q is a counterion which balances the charge of the macrocyclic metal complex on a stoichiometric basis, and
 - L is a further ligand.
- 10 2) an oxidizing agent, and
 - 3) an oxidation-enhancing compound.
- 2. The oxidizing system according to claim 1 which is characterized in that in the general formula (1)

 Y_1 , Y_3 and Y_4 are each independently a $(-CH_2-)_x$ group, where x is 1, 2 or 3 and one or more hydrogen atoms in the $(-CH_2-)_x$ group may be substituted by an R^i radical, R^i being alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy or phenoxy, or two R^i radicals which are bound to two adjacent carbon atoms of the $(-CH_2-)_x$ group combine to form a benzene, cycloalkyl or cycloalkenyl ring which may contain one or more hetero atoms, preferably oxygen, sulfur or nitrogen.

- 25 3. The oxidizing system according to claim 1 or 2 which is characterized in that in the general formula (1)
 - Y₂ is a bridge member having 1, 2 or 3 carbon atoms in the bridge, preferably a (-CH₂-)_y group, where y is 1 or 2 and one or more hydrogen atoms in the (-CH₂-)_x group may be substituted by an Rⁱⁱ radical, Rⁱⁱ being alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy or phenoxy, or two Rⁱⁱ radicals which are bound to two adjacent carbon atoms of the (-CH₂-)_x group combine to form an optionally substituted benzene, cycloalkyl or

cycloalkenyl ring which may contain one or more hetero atoms, preferably oxygen, sulfur or nitrogen, preferably a benzene ring which may be substituted by electron-donating or electron-withdrawing radicals.

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4. The oxidizing system according to one or more of claims 1-3 which is characterized in that in the general formula (1)

the R radicals are each independently hydrogen, C₁-C₈-alkyl, C₃-C₈-cycloalkyl, C₄-C₁₂-cycloalkenyl, C₂-C₈-alkenyl, C₆-C₁₄-aryl, C₂-C₁₂-alkynyl, C₁-C₁₂-alkylaryl, halogen, alkoxy, phenoxy, CH₂CF₃ or CF₃ or two R radicals which are bound to the same carbon atom combine to form a substituted or unsubstituted benzene, C₃-C₈-cycloalkyl or C₄-C₁₂-cycloalkenyl ring, the carbon atom to which the two R radicals are bound being part of the benzene, cycloalkyl or cycloalkenyl ring.

- 5. The oxidizing system according to one or more of claims 1-4 which is characterized in that in the general formula (1) M represents Cr, Mo, W, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and/or Pt or mixtures of metals of the aforementioned oxidation states or from the identified groups of the periodic table.
- 6. The oxidizing system according to one or more of claims 1-5 which is characterized in that in the general formula (1) Q is an alkali metal counterion, preferably potassium, lithium or sodium, NRⁱⁱⁱ₄⁺ or PRⁱⁱⁱ₄⁺, where every Rⁱⁱⁱ is independently hydrogen, alkyl, aryl, alkylaryl, alkenyl or joins to form a cycloalkyl, cycloalkenyl or an aryl ring which optionally contains one or more hetero atoms, preferably oxygen, sulfur or nitrogen.
- 7. The oxidizing system according to one or more of claims 1-6 which is characterized in that in the general formula (1) L is a labile ligand, preferably H₂O, Cl or CN.

8. The oxidizing system according to claim 1 which is characterized in that a macrocyclic metal complex used has the general formula (1A)

$$\begin{array}{c|c} & & & \\ & & &$$

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where

X and Z are each independently hydrogen, electron-donating or electron-withdrawing groups,

 R^{iv} and R^{v}

M

are each independently hydrogen, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy or phenoxy radicals or combine to form a cycloalkyl or cycloalkenyl ring which may contain one or more hetero atoms,

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is a transition metal of the oxidation states I, II, III, IV, V or VI or is selected from groups 6, 7, 8, 9, 10 or 11 of the periodic table,

20 Q

is a counterion which balances the charge of the macrocyclic metal complex on a stoichiometric basis, and

L is a further ligand.

25 9. The oxidizing system according to claim 8 which is characterized in that X and Z in the general formula (1A) are each independently halogen, preferably

chlorine, bromine or iodine, SO_3^- , OSO_3^- , OSO_3R^{vi} (where R^{vi} is hydrogen, alkyl, aryl or alkylaryl), NO_2^- , C_1 - C_8 -alkoxy, preferably methoxy, ethoxy, propoxy and butoxy, C_1 - C_8 -alkyl, preferably methyl, ethyl, propyl, n-butyl and tert-butyl, or hydrogen.

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The oxidizing system according to claim 8 or 9 which is characterized in that in the macrocyclic metal complex of the general formula (1A) R^{iv} and R^v are each independently hydrogen, alkyl, preferably C₁-C₅-alkyl, more preferably both identically methyl or ethyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, halogen, alkoxy or phenoxy radicals or combine to form a cycloalkyl ring, especially a cyclopentyl or cyclohexyl ring, or a cycloalkenyl ring, the cycloalkyl or cycloalkenyl ring optionally containing one or more hetero atoms, preferably oxygen, sulfur or nitrogen.

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11. The oxidizing system according to one or more of claims 1-10 which is characterized in that the oxidizing agent comprises hydrogen peroxide, hydrogen peroxide adducts, preferably alkali metal, especially sodium, lithium or potassium, carbonate peroxyhydrate, urea peroxide or compounds capable of releasing or generating hydrogen peroxide in aqueous solution, preferably alkali metal, especially sodium, potassium or lithium perborate (as mono- or tetrahydrate), organic peroxides, preferably benzoyl or cumene hydroperoxides, persulfates, preferably peroxymonosulfate or Carot's acid, perphosphates or persilicates.

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12. The oxidizing system according to one or more of claims 1-11 which is characterized in that the oxidation-enhancing compounds ("mediator") are aliphatic, cycloaliphatic, heterocyclic or aromatic compounds having at least one OH, NO, NOH, HRN-OH functionality or mixtures thereof.

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The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formula (I)

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$$R^2$$
 X
 N
 R^1
 (I)

where X represents (-N=N-), (-N= $\mathbb{C}R^4$ -)_p, (- $\mathbb{C}R^4$ =N-)_p, (- $\mathbb{C}R^5$ = $\mathbb{C}R^6$)_p,

and p is 1 or 2,

where the radicals R¹ to R⁶ be the same or different and each independently denote hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof. amino, nitro, C_1 - C_{12} -alkyl, C_1 - C_6 -alkyloxy, carbonyl-C₁-C₆-alkyl, phenyl, sulfo and also esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and also salts and esters thereof, where the amino, carbamoyl and sulfamoyl groups of the radicals R¹ to R⁶ may be unsubstituted or singly or doubly hydroxyl. C₁-C₃-alkyl or C₁-C₃-alkoxy substituted, and where the radicals R² and R³ may combine to form a conjoint group -A- and -A- is $(-CR^7=CR^8-CR^9=CR^{10}-)$ or $(-CR^{10}=CR^9-CR^8=CR^7-)$, where the radicals R^7 to R¹⁰ are the same or different and each independently denote hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C₁-C₁₂-alkyl, C₁-C₆-alkyloxy, carbonyl-C₁-C₅-alkyl, phenyl, aryl, sulfo and also esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and also salts and esters thereof, where the amino, carbamoyl and sulfamovl groups of the radicals R⁷ to R¹⁰ may be unsubstituted or singly or doubly hydroxyl, C₁-C₃-alkyl or C₁-C₃-alkoxy substituted, and where the C₁-C₁₂-alkyl, C₁-C₆-alkyloxy, carbonyl-C₁-C₆-alkyl, phenyl and aryl groups of the radicals R⁷ to R¹⁰ may be unsubstituted or singly or multiply R¹¹ substituted and where R¹¹ denotes hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C1-C12-alkyl, C₁-C₆-alkyloxy, carbonyl-C₁-C₆-alkyl, phenyl, aryl, sulfo and also esters and

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salts thereof, where the carbamoyl, sulfamoyl and amino groups of the R^{11} radical may be unsubstituted or singly or doubly R^{12} substituted and R^{12} denotes hydrogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C_1 - C_{12} -alkyl, C_1 - C_6 -alkyloxy, carbonyl- C_1 - C_6 -alkyl, phenyl or aryl.

14. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formula (II)

 R^8 X N R^1 (II)

where X represents (-N=N-), (-N= CR^4 -)_p, (- CR^4 =N-)_p, (- CR^5 = CR^6)_p,

and p is 1 or 2

where the radicals R¹ and R⁴ to R¹⁰ are the same or different and denote

hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C_1 - C_{12} -alkyl, C_1 - C_5 -alkyloxy, carbonyl- C_1 - C_6 -alkyl, phenyl, aryl, sulfo and also esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and also salts and esters thereof, where the amino, carbamoyl and sulfamoyl groups of the radicals R^1 and R^4 to R^{10} may be unsubstituted or singly or doubly hydroxyl, C_1 - C_3 -alkyl or C_1 - C_3 -alkoxy substituted and where the C_1 - C_{12} -alkyl, C_1 - C_6 -alkyloxy, carbonyl- C_1 - C_6 -alkyl, phenyl, aryl and aryl- C_1 - C_6 -alkyl groups of the radicals R^1 and R^4 to R^{10} may be unsubstituted or singly or multiply R^{12} substituted

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and where R^{12} denotes hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C_1 - C_{12} -alkyl, C_1 - C_6 -alkyloxy, carbonyl- C_1 - C_6 -alkyl, phenyl, aryl, sulfo, esters and salts thereof, sulfeno, sulfino, where the carbamoyl, sulfamoyl, amino groups of the R^{12} radical may be unsubstituted or singly or doubly R^{13} substituted and where R^{13} denotes hydrogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C_1 - C_{12} -alkyl, C_1 - C_6 -alkyloxy, carbonyl- C_1 - C_6 -alkyl, phenyl or aryl.

15. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formula (III)

$$R^8$$
 N
 N
 $O-R^{14}$
(III)

where X represents (-N=N-), $(-N=CR^4-)_m$, $(-CR^4=N-)_m$, $(-CR^5=CR^6-)_m$,

and m is 1 or 2

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where the radicals R^7 to R^{10} and R^4 to R^6 are each as defined for the formula (II) and

 R^{14} denotes -M, where M denotes hydrogen, alkali, preferably lithium, sodium or potassium, alkaline earth, preferably calcium or magnesium, ammonium, C_1 - C_4 -alkylammonium or C_1 - C_4 -alkanolammonium, C_1 - C_{10} -alkyl, C_1 - C_{10} -alkylcarbonyl, where C_1 - C_{10} -alkyl and C_1 - C_{10} -alkylcarbonyl may be unsubstituted or singly or multiply R^{15} substituted, where R^{15} denotes hydrogen, halogen, hydroxyl, formyl, carboxyl

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and also salts and esters thereof, amino, nitro, C_1 - C_{12} -alkyl, C_1 - C_6 -alkyloxy, carbonyl- C_1 - C_6 -alkyl, phenyl, sulfo, and also esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and also salts and esters thereof, where the amino, carbamoyl and sulfamoyl groups of the R^{15} radical may be unsubstituted or singly or doubly hydroxyl, C_1 - C_3 -alkyl or C_1 - C_3 -alkoxy substituted.

16. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formula (IV)

$$R^{8}$$
 N
 N
 (IV)

where

M denotes hydrogen, alkali, preferably lithium, sodium or potassium, alkaline earth, preferably calcium or magnesium, ammonium, C_1 - C_4 -alkylammonium or C_1 - C_4 alkanolammonium, and

the radicals R⁷ to R¹⁰ are the same or different and each independently denote hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C₁-C₁₂-alkyl, C₁-C₆-alkyloxy, carbonyl-C₁-C₆-alkyl, phenyl, sulfo and also esters and salts thereof, sulfamoyl, carbamoyl, phospho, phosphono, phosphonooxy and also salts and esters thereof, where the amino, carbamoyl and sulfamoyl groups of the radicals R⁷ to R¹⁰ may be unsubstituted or singly or doubly hydroxyl, C₁-C₃-alkyl or C₁-C₃-alkoxy C₁-C₆-alkyloxy, substituted, and where the C_1 - C_{12} -alkyl, carbonyl- C_1 - C_5 -alkyl, phenyl and aryl groups of the radicals R^7 to R^{10} may be unsubstituted or singly or multiply R¹⁶ substituted and where R¹⁶ denotes hydrogen, halogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C₁-C₁₂-alkyl, C₁-C₆-alkyloxy, carbonyl-C₁-C₆-alkyl,

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phenyl, aryl, sulfo, salts or esters thereof, sulfeno, sulfino, where the carbamoyl, sulfamoyl and amino groups of the R^{16} radical may be unsubstituted or singly or doubly R^{17} substituted and R^{17} denotes hydrogen, hydroxyl, formyl, carboxyl and also salts and esters thereof, amino, nitro, C_1 - C_1 -alkyl, C_1 - C_6 -alkyloxy, carbonyl- C_1 - C_6 -alkyl, phenyl or aryl.

17. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are cyclic N-hydroxy compounds comprising at least one five- or six-membered ring containing the structure identified in the general formula (V)

$$\begin{array}{ccc}
B & D \\
II & II \\
-C - N - C - & (V)
\end{array}$$

and also salts, ethers or esters thereof, where

B and D are the same or different and denote oxygen, sulfur or NR¹⁸, where

R¹⁸ represents hydrogen, hydroxyl, formyl, carbamoyl, sulfo, esters or salts sulfamoyl, nitro, amino, phenyl, $aryl-C_1-C_5-alkyl$, C₁-C₁₂-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl, carbonyl-C₁-C₆-alkyl, phospho, phosphono or phosphonooxy and also esters or salts thereof, where the carbamoyl, sulfamoyl, amino and phenyl radicals may be unsubstituted or singly or multiply R¹⁹ substituted and the aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl and carbonyl-C₁-C₆-alkyl radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply R¹⁹ substituted, where R¹⁹ in each occurrence is the same or different and denotes hydroxyl, formyl or carboxyl and also esters or salts thereof, carbamoyl or sulfo, esters or salts thereof, sulfamoyl, nitro, amino, phenyl, C₁-C₅-alkyl or C₁-C₅-alkoxy.

18. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formulae (VI), (VII), (VIII) or (IX)

$$R^{21}$$
 R^{20}
 R^{20}
 R^{20}
 R^{21}
 R^{20}
 R^{21}
 R^{20}
 R^{21}
 R^{20}
 R^{21}
 R^{21}
 R^{22}
 R^{23}
 R^{23}
 R^{23}
 R^{23}
 R^{23}
 R^{23}

where B and D are each as defined for the general formula (V) and the radicals R²⁰-R³⁵ are the same or different and represent halogen, carboxyl and salts or esters thereof or have the meanings defined for R¹⁸, although R²⁶ and R²⁷ on the one hand and R²⁸ and R²⁹ on the other must not both denote hydroxyl or amino and optionally any two of the substituents R²⁰-R²³, R²⁴-R²⁵, R²⁶-R²⁹, R³⁰-R³⁵ may be linked together to form a ring -E-, where -E-

represents

 $(-CH=CH)_n$ with n = 1 to 3, -CH=CH-CH=N- or

- and where optionally the radicals R^{26} - R^{29} may also be bonded together by one or two bridge elements -F-, where -F- in each occurrence is the same or different and has one of the following meanings: -0-, -S, -CH₂-, -CR³⁶=CR³⁷-, where R^{36} and R^{37} are the same or different and have the meaning of R^{20} .
- 10 19. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formulae (VI), (VII), (VIII) or (IX) wherein B and D denote oxygen or sulfur.
- 15 20. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formula (X), (XI) or (XII)

$$G-N-I$$
 (X)

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and also salts, ethers or esters thereof, where

G is a monovalent homo- or heteroaromatic mono- or binuclear radical and

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L is a bivalent homo- or heteroaromatic mono- or binuclear radical and where these aromatic radicals may be substituted by one or more, identical or different R³⁸ radicals, where R³⁸ may represent halogen, hydroxyl, formyl, cyano, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl-C₁-C₅-alkyl, C₁-C₁₂alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl, carbonyl-C₁-C₆-alkyl, phospho, phosphono, phosphonooxy, esters or salts thereof, where the carbamoyl, sulfamoyl, amino and phenyl radicals may in turn be unsubstituted or singly or multiply R³⁹ substituted and the aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl, carbonyl-C₁-C₆-alkyl radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply R³⁹ substituted, where R³⁹ in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl, esters or salts thereof, carbamoyl, sulfo, sulfamoyl, nitro, nitroso, amino, phenyl, C₁-C₅-alkyl, C₁-C₅-alkoxy, C₁-C₅-alkylcarbonyl and two R³⁸ or R³⁹ radicals at a time may be linked together pairwise via a [-CR⁴⁰R⁴¹-]_m bridge, where m is 0.1.2, 3 or 4, and R⁴⁰ and R⁴¹ are the same or different and denote carboxyl, phenyl, C₁-C₅-alkyl, or salts thereof, C₁-C₅-alkoxy esters C₁-C₅-alkylcarbonyl and one or more nonadjacent [-CR⁴⁰R⁴¹-] groups may be replaced by O, S or an optionally C₁-C₅-alkyl-substituted imino radical and two adjacent [-CR⁴⁰R⁴¹-] groups by a [-CR⁴⁰=CR⁴¹] group and denotes a monovalent acid radical present in amidic form of acids selected from the group consisting of carboxylic acids having up to 20 carbon atoms, carbonic acid, half esters of carbonic acid or of carbamic acid, sulfonic acid, phosphonic acid, phosphoric acid, monoesters of phosphoric acid, and diesters of phosphoric acid and K is a divalent acid radical present in amidic form of acids selected from the group consisting of mono- and dicarboxylic acids having up to 20 carbon atoms, carbonic acid, sulfonic acid, phosphonic acid, phosphoric acid or monoesters of phosphoric acid.

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21. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formula (XIII), (XIV), (XV), (XVI) or (XVII)

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 Ar^2

and also salts, ethers or esters thereof, where

Ar¹ denotes a univalent homo- or heteroaromatic mononuclear aryl radical and

denotes a bivalent homo- or heteroaromatic mononuclear aryl radical which may each be substituted by one or more, identical or different R⁴⁴ radicals, where R⁴⁴ represents hydroxyl, cyano, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, nitro, nitroso, amino, C₁-C₁₂-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl, carbonyl or C₁-C₆-alkyl, where the amino radicals may be unsubstituted or singly or multiply R⁴⁵ substituted and the C₁-C₅-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl and carbonyl-C₁-C₆-alkyl radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply R⁴⁵ substituted, where R⁴⁵ in each occurrence is the same or different and denotes hydroxyl, carboxyl, esters or salts thereof, sulfo, nitro, amino, C₁-C₅-alkyl, C₁-C₅-alkoxy or C₁-C₅-alkylcarbonyl and two R⁴⁴ radicals

at a time may be linked together pairwise via a $[-CR^{40}R^{41}-]_m$ bridge where m is 0, 1, 2, 3 or 4, and where

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 R^{40} and R^{41} are each as defined in claim 19 and one or more nonadjacent [-CR⁴⁰R⁴¹-] groups may be replaced by O, S or an optionally C₁-C₅-alkyl-substituted imino radical and two adjacent [-CR⁴⁰R⁴¹-] groups may be replaced by a [-CR⁴⁰=CR⁴¹-] group, and where

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 R^{42} in each occurrence is the same or different and denotes hydrogen, phenyl, aryl- C_1 - C_5 -alkyl, C_1 - C_{12} -alkyl, C_1 - C_5 -alkoxy or C_1 - C_{10} -carbonyl, where the phenyl radicals may be unsubstituted or singly or multiply R^{46} substituted and the aryl- C_1 - C_5 -alkyl, C_1 - C_1 -alkyl, C_1 - C_5 -alkoxy, C_1 - C_5 -carbonyl radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply R^{46} substituted, where

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 R^{46} in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl, esters or salts thereof, carbamoyl, sulfo, sulfamoyl, nitro, nitroso, amino, phenyl, C_1 - C_5 -alkyl or C_1 - C_5 -alkoxy and R^{43} denotes divalent radicals ortho-, meta-, para-phenylene, aryl- C_1 - C_6 -alkyl, C_1 - C_1 -alkylene or C_1 - C_5 -alkylenedioxy, where the phenylene radicals may be unsubstituted or singly or multiply R^{46} substituted and the aryl- C_1 - C_5 -alkyl, C_1 - C_1 -alkyl and C_1 - C_5 -alkoxy

radicals may be saturated or unsaturated, branched or unbranched and

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p denotes 0 or 1 and

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q denotes an integer from 1 to 3.

may be singly or multiply R⁴⁶ substituted, where

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The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formula (XVIII) or (XIX),

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and also salts, ethers or esters thereof, where

M in each occurrence is the same or different and denotes a univalent linear or branched, cyclic or polycyclic, saturated or unsaturated C1-C2-alkvl radical and where this alkyl radical may be substituted by one or more R⁴⁸ radicals, where R⁴⁸ in each occurrence is the same or different and denotes hydroxyl, mercapto, formyl, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, amino, hydroxylamino, phenyl, C_1 - C_5 -alkoxy, C_1 - C_{10} -carbonyl, phospho, phosphono or phosphonooxy and also esters or salts and where the carbamoyl, sulfamoyl, amino, hydroxylamino, mercapto and phenyl radicals may be unsubstituted or singly or multiply R⁴⁸ substituted and the C₁-C₅-alkoxy and C₁-C₁₀-carbonyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R⁴⁸ substituted, where R⁴⁸ in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl, esters or salts thereof, carbamoyl, sulfo, salts or esters thereof, sulfamoyl, nitro, nitroso, amino, phenyl, benzoyl, C₁-C₅-alkyl, C₁-C₅-alkoxy or C₁-C₅-alkylcarbonyl and non-α-disposed methylene groups may be replaced by O, S or an optionally monosubstituted imino radical, and

N'" denotes a monovalent acid radical in amidic form of acids which are aliphatic, mono- or binuclear aromatic or mono- or binuclear heteroaromatic carboxylic acids having 1-20 carbon atoms, carbonic acid, half esters of carbonic acid or of carbamic acid, sulfonic acid, phosphoric acid, phosphoric acid, monoesters of phosphoric acid or diesters of phosphoric acid, and

T denotes a bivalent acid radical in amidic form of acids which are aliphatic, mono- or binuclear aromatic or mono- or binuclear heteroaromatic

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dicarboxylic acids having 1-20 carbon atoms, carbonic acid, sulfonic acid, phosphonic acid, phosphoric acid or monoesters of phosphoric acid, and where alkyl radicals of the aliphatic acids N" and T which are present in amidic form may be linear or branched, cyclic and/or polycyclic, saturated or unsaturated and contain 1-24 carbon atoms and are unsubstituted or singly or multiply R⁴⁷ substituted and where, furthermore, aryl and heteroaryl radicals of the aromatic or heteroaromatic acids N" and T which are present in amidic form may be substituted by one or more R⁴⁹ radicals, where R⁴⁹ may be substituted, in which case R⁴⁹ in each occurrence is the same or different and denotes hydroxyl, mercapto, formyl, cyano, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl- C_1 - C_5 -alkyl, C_1 - C_{12} -alkyl, C_1 - C_5 -alkoxy, C_1 - C_{10} -carbonyl, phospho, phosphono or phosphonooxy and also esters or salts thereof and where the carbamoyl, sulfamoyl, amino, mercapto and phenyl radicals may be unsubstituted or singly or multiply R⁴⁸ substituted and the aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl-C₁-C₅-alkoxy, C₁-C₁₀-carbonyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R⁴⁸ substituted.

20 23. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formulae (XX), (XXI), (XXII) or (XXIII)

$$Alk^{1} \xrightarrow{N} C \xrightarrow{R^{52}} (XX)$$

$$Alk^{1} \xrightarrow{N} (R^{54})_{p} \xrightarrow{N} Alk^{1} (XXI)$$

$$Alk^{1} \xrightarrow{N} R^{52} (XXII)$$

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$$\begin{array}{c} OH \\ I \\ R^{52} \\ N \downarrow I \\ P \end{array} \qquad (XXIII)$$

and also salts, ethers or esters thereof, where

Alk in each occurrence is the same or different and denotes a univalent linear or branched, cyclic or polycyclic, saturated or unsaturated C₁-C₁₀-alkyl radical,

where this alkyl radical may be substituted by one or more R^{50} radicals, where R^{50} in each occurrence is the same or different and denotes hydroxyl, formyl, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, amino, hydroxylamino, phenyl, C_{l} - C_{5} -alkoxy, C_{1} - C_{5} -carbonyl and where the carbamoyl, sulfamoyl, amino, hydroxylamino and phenyl radicals may be unsubstituted or singly or multiply R^{51} substituted and the C_{l} - C_{5} -alkoxy and C_{l} - C_{10} -carbonyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R^{51} substituted, where

 R^{51} in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl, esters or salts thereof, carbamoyl, sulfo, salts or esters thereof, sulfamoyl, nitro, amino, phenyl, benzoyl, C_I - C_5 -alkyl, C_I - C_5 -alkoxy or C_I - C_5 -alkylcarbonyl and non- α -disposed methylene groups may be replaced by O, S or an optionally monosubstituted imino radical, and where

 R^{52} denotes identical or different univalent radicals hydrogen, phenyl, pyridyl, furyl, pyrrolyl, thienyl, aryl C_l - C_5 -alkyl, C_l - C_{12} -alkyl, C_l - C_{10} -alkoxy or C_l - C_{10} -carbonyl, where the phenyl, pyridyl, furyl, pyrrolyl and thienyl radicals may be unsubstituted or singly or multiply R^{53} substituted and the aryl- C_l - C_5 -alkyl, C_l - C_{12} -alkyl, C_l - C_5 -alkoxy and C_l - C_{10} -carbonyl radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply R^{53} substituted, where

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R⁵³ in each occurrence is the same or different and denotes hydroxyl, formyl, carboxyl, esters or salts thereof, carbamoyl, sulfo, esters and salts thereof, sulfamoyl, nitro, amino, phenyl, C₁-C₅-alkyl or C₁-C₅-alkoxy, and

R⁵⁴ denotes bivalent radicals phenylene, pyridylene, thienylene, furylene, pyrrolylene, aryl-C₁-C₅-alkyl, C₁-C₁₂-alkylene, C₁-C₅-alkylenedioxy, where phenylene, pyridylene, thienylene, furylene and pyrrolylene may be unsubstituted or singly or multiply R⁵³ substituted and the aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl, C₁-C₅-alkoxy radicals may be saturated or unsaturated, branched or unbranched and may similarly be singly or multiply R⁵³ substituted, where p denotes 0 or 1.

24. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formulae (XXIV) or (XXV)

and also salts, ethers or esters thereof, where

U in each occurrence is the same or different and denotes oxygen, sulfur or NR⁵⁵, where

25 R⁵⁵ denotes hydrogen, hydroxyl, formyl, carbamoyl, sulfo, esters or salts thereof, sulfamoyl, nitro, amino, phenyl, aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl,

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C₁-C₅-alkoxy, C₁-C₁₀-carbonyl, carbonyl-C₁-C₆-alkyl, phospho, phosphono or phosphonooxy and also esters or salts thereof,

where the carbamoyl, sulfamoyl, amino and phenyl radicals may be unsubstituted or singly or multiply R^{56} substituted and the aryl- C_1 - C_5 -alkyl, C_1 - C_{10} -alkyl, C_1 - C_5 -alkoxy, C_1 - C_{10} -carbonyl and carbonyl- C_1 - C_6 -alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R^{56} substituted, where

10 R⁵⁶ in each occurrence is the same or different and denotes hydroxyl, formyl, carboxyl, esters or salts thereof, carbamoyl, sulfo, esters or salts thereof, sulfamoyl, nitro, amino, phenyl, C₁-C₅-alkyl or C₁-C₅-alkoxy, and

the radicals R⁵⁷ and R⁵⁸ are the same or different and denote halogen or carboxyl and also esters or salts thereof, or have the meanings defined for R⁵⁵, or are linked together to form a [-CR⁶¹R⁶²]_n ring, where n is 2, 3 or 4, and

 R^{59} and R^{60} have the meanings defined for R^{55} , and

20 R⁶¹ and R⁶² are the same or different and denote halogen or carboxyl and also esters or salts thereof, or have the meanings defined for R⁵⁵.

25. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formulae (XXVI) or (XXVII)

$$R^{63}$$
 R^{64}
 R^{66}
 R^{66}
 R^{65}
 R^{66}
 R^{66}
 R^{65}
 R^{66}
 R^{66}
 R^{67}
 R^{68}
 R^{68}
 R^{68}
 R^{68}

and also salts, ethers or esters thereof, where

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 R^{63} , R^{64} , R^{65} and R^{66} are the same or different and denote hydrogen, halogen, hydroxyl, formyl, carbamoyl or carboxyl and also esters or salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, cyano, amino, phenyl, aryl- C_l - C_5 -alkyl, C_l - C_{12} -alkyl, C_l - C_5 -alkoxy, C_l - C_{10} -carbonyl, carbonyl- C_l - C_6 -alkyl, phospho, phosphono or phosphonooxy and also esters or salts thereof, where the carbamoyl, sulfamoyl, amino and phenyl radicals may be unsubstituted or singly or multiply R^{67} substituted and the aryl- C_l - C_5 -alkyl, C_l - C_{12} -alkyl, C_l - C_5 -alkoxy, C_l - C_{10} -carbonyl, carbonyl- C_l - C_6 -alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R^{67} substituted, where

 R^{67} in each occurrence is the same or different and denotes hydroxyl, formyl or carboxyl and also esters or salts thereof, carbamoyl, sulfo, salts or esters thereof, sulfamoyl, nitro, nitroso, amino, phenyl, C_1 - C_5 -alkyl or C_1 - C_5 -alkoxy or the R^{63} , R^{64} , R^{65} and R^{66} radicals are linked together pairwise to form a $[-CR^{68}R^{69}-]_m$ ring, where m is an integer from 1 to 4, or to form a $[-CR^{70}=CR^{71}-]_n$ ring, where n is an integer from 1 to 3, and

 R^{68} , R^{69} , R^{70} and R^{71} are the same or different and have the meanings defined for R^{63} to R^{66} .

26. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formulae (XXVIII), (XXIX) or (XXX)

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$$R^{72}$$
 R^{72}
 R^{72}

and also tautomers, salts, ethers or esters thereof, where in the formulae (XXVIII), (XXIX) and (XXX) two mutually ortho- or para-disposed R⁷² radicals denote hydroxyl and nitroso or hydroxyl and mercapto or nitroso and amino and the other R72 radicals are the same or different and denote hydrogen, halogen, hydroxyl, mercapto, formyl, cyano, carbamoyl or carboxyl and also esters and salts thereof, sulfo, esters and salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl, carbonyl-C₁-C₆-alkyl, phospho, phosphono or phosphonooxy and also esters and salts thereof and where the carbamoyl, sulfamoyl, amino, mercapto and phenyl radicals may be unsubstituted or singly or multiply R⁷³ substituted and the aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl, carbonyl-C₁-C₆-alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R⁷³ substituted, where R⁷³ in each occurrence is the same or different and denotes hydroxyl, formyl, cyano or carboxyl and also esters or salts thereof, carbamoyl, sulfo, sulfamoyl, nitro, nitroso, amino, phenyl, C_1 - C_5 -alkyl, C_1 - C_5 -alkoxy or C_1 - C_5 -alkylcarbonyl and two R^{72} radicals at a time or two R⁷³ radicals at a time or R⁷² and R⁷³ may be linked together pairwise via a $[-CR^{74}R^{75}-]_m$ bridge, where m is 1, 2, 3 or 4, and R^{74} and R^{75} are the same or different and denote carboxyl, esters or salts thereof, phenyl, C₁-C₅-alkyl, C₁-C₅-alkoxy or C₁-C₅-alkylcarbonyl and one or more nonadjacent [-CR⁷⁴R⁷⁵-] groups may be replaced by O, S or an optionally C₁-C₅-alkylsubstituted imino radical and two adjacent [-CR⁷⁴R⁷⁵-] groups may be replaced by one [-CR⁷⁴=R⁷⁵-] group.

27. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formulae (XXXI), (XXXII) or (XXXIII)

$$Ar = N - Ar$$
 (XXXII)

 $Ar = N - C - R^{76}$
 $R^{76} = C - N - C - R^{76}$
 $R^{76} = C - N - C - R^{76}$
 $R^{76} = C - N - C - R^{76}$
 $R^{76} = C - N - C - R^{76}$
 $R^{76} = C - N - C - R^{76}$

(XXXIII)

5 where

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Ar is a univalent homo- or heteroaromatic mono- or binuclear radical and where this aromatic radical may be substituted by one or more, identical or different R⁷⁷ radicals, where R⁷⁷ denotes halogen, formyl, cyano, carbamoyl, carboxyl, esters or salts thereof, sulfo, esters or salt thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl, carbonyl-C₁-C₆-alkyl, phospho, phosphono or phosphonooxy and also esters or salts thereof, and

where the phenyl, carbamoyl and sulfamoyl radicals may be unsubstituted or singly or multiply R⁷⁸ substituted, the amino radical may be singly or doubly R⁷⁸ substituted and the aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl, carbonyl-C₁-C₆-alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R⁷⁸ substituted,

where R^{78} may occur one or more times and in each occurrence is the same or different and denotes hydroxyl, formyl, cyano or carboxyl and also esters or salts thereof, carbamoyl, sulfo and also esters and salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, C_1 - C_5 -alkyl, C_1 - C_5 -alkoxy or C_1 - C_5 -alkylcarbonyl, and

R⁷⁶ in each occurrence is the same or different and denotes halogen, hydroxyl, mercapto, formyl, cyano, carbamoyl, carboxyl and also esters or

salts thereof, sulfo, esters or salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, aryl- C_1 - C_5 -alkyl, C_1 - C_1 -alkyl, C_1 - C_5 -alkoxy, C_1 -10-carbonyl, carbonyl- C_1 - C_6 -alkyl, phospho, phosphono or phosphonooxy and also esters or salts thereof, and

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R⁷⁶ may also denote hydrogen in the case of bicyclic stable nitroxyl free radicals (structure XXXIII), and

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where the carbamoyl, sulfamoyl, amino, mercapto and phenyl radicals may be unsubstituted or singly or multiply R⁷⁹ substituted and the aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl, carbonyl-C₁-C₆-alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R⁷⁹ substituted, where R⁷⁹ in each occurrence is the same or different and denotes hydroxyl, formyl, cyano, carboxyl, esters or salts thereof, carbamoyl, sulfo, esters and salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, C₁-C₅-alkyl, C₁-C₅-alkoxy or C₁-C₅-alkylcarbonyl and two R⁷⁸ or R⁷⁹ radicals at a time may be linked together pairwise via a [-CR⁸⁰R⁸¹-]_m bridge, where m is 0, 1, 2, 3 or 4, and

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 R^{80} and R^{81} are the same or different and denote halogen, carboxyl and also esters or salts thereof, carbamoyl, sulfamoyl, phenyl, benzoyl, C_1 - C_5 -alkyl, C_1 - C_5 -alkoxy or C_1 - C_5 -alkylcarbonyl and one or more nonadjacent [- $CR^{80}R^{81}$ -] groups may be replaced by O, S or an optionally C_1 - C_5 -alkyl-substituted imino radical and two adjacent [- $CR^{80}R^{81}$ -] groups may be replaced by one [- CR^{80} = CR^{81} -], [- CR^{80} =N-] or [- CR^{80} =N(O)-] group.

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28. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formulae (XXXIV) and (XXXV)

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where

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 R^{82} in each occurrence is the same or different and denotes phenyl, aryl- C_1 - C_5 -alkyl, C_1 - C_{12} -alkyl, C_1 - C_5 -alkoxy, C_1 - C_{10} -carbonyl or carbonyl- C_1 - C_6 -alkyl, where the phenyl radicals may be unsubstituted or singly or multiply R^{84} substituted and the aryl- C_1 - C_5 -alkyl, C_1 - C_{12} -alkyl, C_1 - C_5 -alkoxy, C_1 - C_{10} -carbonyl and carbonyl- C_1 - C_6 -alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or multiply R^{84} substituted, where R^{84} may occur one or more times and in each occurrence is the same or different and denotes hydroxyl, formyl or carboxyl and also esters or salts thereof, carbamoyl, sulfo and also esters and salts thereof, sulfamoyl, nitro, nitroso, amino, phenyl, benzoyl, C_1 - C_5 -alkyl, C_1 - C_5 -alkylcarbonyl, and

R⁸³ in each occurrence is the same or different and denotes hydrogen, hydroxyl, mercapto, formyl, cyano, carbamoyl, carboxyl and also esters or salts thereof, sulfo and also esters or salts thereof, sulfamoyl, nitro, nitroso, aryl-C₁-C₅-alkyl, amino, phenyl, C_1 - C_{12} -alkyl, C₁-C₅-alkoxy, C_1 - C_{10} -carbonyl, carbonyl-C₁-C₆-alkyl, phospho, phosphono phosphonooxy and also esters or salts thereof, where the carbamoyl, sulfamoyl, amino, mercapto and phenyl radicals may be unsubstituted or singly or multiply R⁷⁸ substituted and the aryl-C₁-C₅-alkyl, C₁-C₁₂-alkyl, C₁-C₅-alkoxy, C₁-C₁₀-carbonyl and carbonyl-C₁-C₆-alkyl radicals may be saturated or unsaturated, branched or unbranched and may be singly or · 5

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multiply R^{78} substituted and one [-CR⁸³R⁸³-] group may be replaced by O, an optionally C₁-C₅-alkyl-substituted imino radical, a (hydroxy)imino radical, a carbonyl function or an optionally R^{78} mono- or disubstituted vinylidene function and two adjacent [-CR⁸³R⁸³-] groups may be replaced by one [-CR⁸³-CR⁸³-] or [-CR⁸³=N-] or [-CR⁸³=N(O)-] group.

29. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds are compounds of the general formulae (XXXVI):

HO—A (XXXVI)

where

A denotes a -D, -CH=CH-D, -CH=CH-CH=CH-D, -CH=N-D, or -N=CH-D group, where D denotes a -CO-E, -SO₂-E, -N-XY or -N⁺-XYZ group wherein E denotes either hydrogen, hydroxyl, a -R or -OR radical and X, Y and Z are the same or different and hydrogen or likewise a -R radical, where R is a C₁-C₁₆-alkyl radical, preferably a C₁-C₈-alkyl radical, and alkyl is in each case saturated or unsaturated, straight-chain or branched and optionally carboxyl, sulfo or amino substituted; and

B and C are the same or different and represent a C_mH_{2m+1} group where $1 \le m \le 5$.

30. The oxidizing system according to one or more of claims 1-12 which is characterized in that the oxidation-enhancing compounds comprise one of the following compounds:

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| ts thereof, |
|-------------|
| ts thereof, |
| ts thereof, |
| ts thereof, |
| lts thereof |
| lts thereof |
| lts thereof |
| lts thereof |
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2-nitroso-l-naphthol-3-sulfonic acid,

1-nitroso-2-naphthol-3,6-disulfonic acid, and methyl syringate.

- 31. A process for oxidizing oxidizable substances which is characterized in that the oxidizable substance is contacted with an oxidizing system according to one or more of claims 1-30.
- 32. A process for removing excess, unfixed dye from textile materials after a dyeing, preferably after a reactive dyeing, the process being characterized in that the dyed textile material is contacted with an oxidizing system according to one or more of claims 1-30 in at least one of the post-dyeing rinse steps.
- 33. The process according to claim 32 which is characterized in that the dyed textile material is contacted with the oxidizing system in at least one of the post-dyeing rinse steps by at least one of the rinse liquors having added to it
 - the three components of the oxidizing system individually in any desired order in succession or else individually and concurrently, or
- 2) initially the two components of the macrocyclic metal complex and of the oxidation-enhancing compound either individually and concurrently or else as a conjoint formulation and subsequently the oxidizing agent or
- 3) initially the two components of the oxidizing agent and of the oxidation-enhancing compound either individually and concurrently or else as a conjoint formulation and subsequently the macrocyclic metal complex.
- 30 34. Dyed textile material obtainable by the process according to claim 32 or 33.
 - 35. A process for removing colored impurities from industrial wastewater, preferably from wastewater of the paper- or textile-processing industry, the process being characterized in that the industrial wastewater is contacted with

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an oxidizing system according to one or more of claims 1 to 30.

- 36. Wastewater, preferably wastewater of the paper- or textile-processing industry, obtainable by the process according to claim 35.
- 37. A process for lightening colored impurities on solid materials, preferably on textiles, paper or leather, the process being characterized in that the solid materials are contacted with an oxidizing system according to one or more of claims 1 to 30.
- 38. Solid materials, preferably textiles, paper or leather, obtainable by the process according to claim 37.